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SOME SUGGESTIONS ON THE SAFE USE OF REFRIGERANTS

BY

H. H. SCHRENK

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

SOME SUGGESTIONS ON THE SAFE USE OF REFRIGERANTS[1/]

By H. H. Schrenk[2/]

The safe use of a refrigerant or any substance depends on knowledge of its pertinent properties and conditions of use; therefore some of the properties of refrigerants that are related to life, fire, and explosion hazards are discussed herein. These data serve as a basis for suggested control measures in the use of refrigerants.

The properties of refrigerants may be broadly classified into three main groups: (1) Those important for refrigeration, (2) those significant from the standpoint of confining the refrigerant, and (3) those that become important if the refrigerant escapes from the machine or container.

The first group of properties, such as latent heat of vaporization, specific heat of vapor, specific heat of liquid, etc., is not considered to be directly related to safety and is not discussed here.

The second group, those properties important in confining the refrigerants, has particular significance because it relates to "built-in" safety. This group is emphasized because it is believed the soundest procedure in designing equipment is to give due consideration to both the health and safety hazards likely to be associated with the equipment. Furthermore, the toxicity, fire, and explosion hazards are controlled as long as the refrigerant is confined. Some properties of this group are (1) stability, (2) corrosiveness, (3) boiling point, (4) pressure developed in the system, (5) warning odor or irritation, and (6) ease of detection.

The third group includes such properties as toxicity (of compound and decomposition products), irritating action, and explosibility.

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SUBSTANCES USED AS REFRIGERANTS

Many substances have been suggested and tried as refrigerants, but the number used more or less extensively is limited. Table 1 is a list of refrigerants that are included in the American Standard Safety Code for Mechanical Refrigeration B9-1939.3/

TABLE 1. - Common refrigerants

Name	Formula	Mol. wt.
Ammonia	NH_3	17.03
Carbon dioxide	CO_2	44.01
Methyl formate	$HCOOCH_3$	60.05
Sulfur dioxide	SO_2	64.06
Ethane	C_2H_6	30.07
Propane	C_3H_8	44.08
Butane	C_4H_{10}	58.12
Isobutane	$(CH_3)_3CH$	58.12
Methyl chloride	CH_3Cl	50.49
Ethyl chloride	C_2H_5Cl	64.52
Dichloromethane (Carrene No. 1)	CH_2Cl_2	84.94
Dichloroethylene	$C_2H_2Cl_2$	96.92
Dichloromonofluoromethane (Freon-21)	$CHCl_2F$	102.93
Dichlorodifluoromethane (Freon-12)	CCl_2F_2	120.92
Trichloromonofluoromethane (Freon-11)	CCl_3F	137.38
Dichlorotetrafluoroethane (Freon-114)	$C_2Cl_2F_4$	170.93

The compounds are listed in four main groups: (1) Miscellaneous, (2) hydrocarbons of the methane series, (3) chlorinated hydrocarbons, and (4) chlorofluorohydrocarbon compounds.

Molecular weights are given because of their relationship to weight of gas per unit volume. The molecular weight of air, calculated upon the basis of its composition, is approximately 29. Any gas having a molecular weight less than this is lighter than air, and any gas with a higher molecular weight is heavier than air. Expressing it another way, the higher the molecular weight the less gas is formed per unit of weight; that is, 1 pound of ammonia will produce about 23 cubic feet of gas at 25° C. and 760 mm., while 1 pound of Freon-114 will produce 2.3 cubic feet of gas.

3/ American Standard Safety Code for Mechanical Refrigeration: Refrig. Eng., vol. 37, suppl. to June 1939 issue.

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PROPERTIES RELATED TO CONFINING REFRIGERANTS

Table 2 gives some properties of refrigerants that are significant in connection with their confinement in a mechanical system.

TABLE 2. - Properties related to confining refrigerants

Refrigerant	Boiling point, °F.	Head pressure at 86°F.[1]	Suction pressure at 5°F.[1]	Corrosive[2]	Warning odor or irritation	Readily detected
Dichloroethylene	119.12	-	-	No	No	Yes
Dichloromethane	104.	[3]9.4	[3]27.3	No	No	Yes
Methyl formate	89.6	[3]1.8	[3]26.3	Yes	Slight	No
Freon-11	74.67	3.6	[3]23.9	No	No	Yes
Ethyl chloride	55.6	12.4	[3]20.5	No	No	Yes
Freon-21	48.0	16.5	[3]19.3	No	No	Yes
Freon-114	38.5	21.1	[3]15.3	No	No	Yes
Butane	30.9	26.9	[3]13.2	No	No	No
Sulfur dioxide	14.0	51.8	[3] 5.9	Yes	Strong	Yes
Isobutane	14.0	44.8	[3] 3.3	No	No	No
Methyl chloride	-11.36	80.8	6.2	No	No	Yes
Freon-12	-21.7	93.2	11.3	No	No	Yes
Ammonia	-28.03	154.5	19.6	Yes	Strong	Yes
Propane	-44.	140.6	27.4	No	No	No
Carbon dioxide	-108.4	1024.3	319.7	No	No	No
Ethane	-127.5	-	-	No	No	No

1/ Pounds per square inch gage.
2/ It is difficult to give a yes or no answer on corrosiveness as moisture has a marked effect in some instances and the kind of metal also is important.
3/ Inches of mercury below atmospheric pressure.

The refrigerants listed in table 2 are arranged in accordance with decreasing boiling point, which in general tends to parallel the pressure developed in the system. Materials suitable to withstand such pressures must be chosen, as the greater the pressure the greater the possibility of leaks as well as rupture of pipes and joints. Compounds having low boiling points operate at pressures exceeding atmospheric on both high- and low-pressure sides, and all leaks are outward. Those with high boiling points may operate on a negative pressure on both the high and the low side or only on the low side. Should leaks occur, the escape of refrigerant would be much slower than for those compounds that have a low boiling point and are gases at ordinary room temperature and pressure. Prevention of leaks is necessary not only because of hazard to health and safety but also to overcome operation difficulties.

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Corrosiveness is one of the most important properties of refrigerants, not only from the standpoint of safety but also of operation. It is not surprising, therefore, that virtually all the common refrigerants are noncorrosive, particularly in the absence of moisture. Ammonia will attack copper and brass, but apparently even these metals will stand up in piston rings, rods, and bearings that are protected by a film of oil. Aqua ammonia has virtually no effect on steel or iron pipe. Although noncorrosive when dry, sulfur dioxide is quite reactive in the presence of moisture.

The halogenated hydrocarbons containing either chlorine or fluorine, or both, in general have low corrosiveness even in the presence of moisture, the fluorine derivatives being the more stable. As halogenated hydrocarbons are good solvents for organic substances, gaskets may be attacked.

The fact that leaks are undesirable emphasizes the importance of their detection. Sulfur dioxide and ammonia have excellent warning properties and, although desirable from the standpoint of detecting leaks, may be objectionable because of excessive irritation. The halogenated hydrocarbons can be detected with the so-called halide lamp, which utilizes copper to give a green flame in the presence of halogens. The use of warning agents has been suggested, and acrolein has been used with methyl chloride. Carbon dioxide and the hydrocarbons ethane, propane, butane, and isobutane are not readily detected in low concentrations.

INFLAMMABILITY OF REFRIGERANTS

Table 3 gives the upper and lower explosive limits of the refrigerants listed in table 1.

Of the common refrigerants, sulfur dioxide, carbon dioxide, and the Freon group are nonexplosive. The chlorinated hydrocarbons dichloroethylene, methyl chloride, and ethyl chloride are all explosive, as are methyl formate and ammonia. The aliphatic hydrocarbons ethane, propane, butane, and isobutane are very explosive. The importance attached to the explosion hazard of this latter group is evidenced by the fact that they are classified in group 3 of the American Standard Safety Code for Mechanical Refrigeration, previously mentioned. Group 1 is considered the least hazardous and group 2 intermediate.

PHYSIOLOGICAL EFFECTS OF REFRIGERANTS

The physiological effects of refrigerants may be divided into three types - (1) local effects, (2) acute, systemic effects, and (3) chronic effects. Consideration also must be given to decomposition products as well as to the effects of the compound itself.

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TABLE 3. - Explosive limits of common refrigerants

Compound	Explosive limits, percent by volume	
	Lower	Upper
Ammonia	16	25
Carbon dioxide	1/	1/
Methyl formate	5	22.7
Sulfur dioxide	1/	1/
Ethane	3.2	12.5
Propane	2.4	9.5
Butane	1.9	8.4
Isobutane	1.8	8.4
Methyl chloride	8.2	18.7
Ethyl chloride	4	14.8
Dichloromethane	2/	2/
Dichloroethylene	5.6	11.4
Dichloromonofluoromethane	2/	2/
Dichlorodifluoromethane	1/	1/
Trichloromonofluoromethane	1/	1/
Dichlorotetrafluoroethane	1/	1/

1/ Nonexplosive.

2/ Virtually nonexplosive at ordinary temperatures, but at higher temperatures under favorable laboratory test conditions it is capable of forming weakly combustible mixtures with air.

Local effects. - Local effects, such as those produced by freezing, may occur with any of the low-boiling refrigerants should they come in contact with the skin or mucous membranes in appreciable amounts when in the liquid state. From the standpoint of chemical action, only ammonia and sulfur dioxide are significant. Both compounds are extremely irritating to the eyes, mucous membranes, and skin.

Acute toxicity. - The hazard of acute toxicity of the hydrocarbons ethane, propane, butane, and isobutane may be considered virtually nonexistent. Ethane usually is classed as physiologically inert, and although the physiological activity in this series of compounds increases with increase in number of carbon atoms, the physiological activity of butane is very slight and certainly has no practical significance in comparison with the explosion hazard.

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Dichlorodifluoromethane (Freon-12), dichlorotetrafluoroethane (Freon-114), dichloromonofluoromethane (Freon-21), and trichloromonofluoromethane (Freon-11, Carrene No. 2) are of a low order of toxicity. Of these compounds, Freon-12 and Freon-114 are the least toxic of the fluorine derivatives listed, Freon-11 and Freon-21 being slightly more toxic.

Carbon dioxide is of a low order of toxicity but is not physiologically inert, as is sometimes stated. It has a definitely stimulating effect on the respiratory system. Increased ventilation of the lungs is produced by even 0.5 percent carbon dioxide, but a concentration of about 3.5 percent is necessary before one is definitely conscious of increased respiratory effort. One can continue to work for a protracted period at a concentration of 5 percent, but most persons probably would be incapacitated by concentrations greater than 6 percent. Recovery generally is rapid on removal to fresh air.

The acute toxicity of dichloromethane (Carrene No. 1) and ethyl chloride is about the same, both being somewhat more toxic than the Freon group. The acute toxicity of dichloroethylene is rated[4/] slightly greater than that of dichloromethane and ethyl chloride.

Ammonia and sulfur dioxide are highly toxic and extremely irritating. Methyl chloride also is definitely toxic.

Chronic toxicity. - Information on chronic effects of the refrigerants is not as complete or as easily interpreted as the acute toxicity. However, from experience and available data it would seem that little or no difficulty should be experienced with carbon dioxide, ethane, propane, butane, isobutane, and the members of the Freon group listed.

Chronic poisoning or physiological effects from repeated mild exposures have been reported for methyl chloride. Repeated exposure to ethyl chloride, dichloroethylene, and dichloromethane also might be expected to produce physiological changes but probably not to the same extent as methyl chloride. Ammonia and sulfur dioxide also produce chronic effects on repeated exposure. In all instances of chronic effects two factors are necessary - (1) sufficiently high concentration and (2) a sufficient number of exposures.

Decomposition products. - All halogenated compounds decompose when subjected to enough heat to form halogenated acids such as hydrochloric and hydrofluoric acids. These acids are both irritating and toxic. The possibility

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4/ Nuckolls, A. H., The Comparative Life, Fire, and Explosion Hazards of Common Refrigerants: Underwriters' Lab. Misc. Hazard Rept. 2375, 1933.

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of high concentrations is not great for most situations, inasmuch as it is necessary not only that the refrigerant and source of heat be present together but also that there be circulation to keep undecomposed refrigerant in contact with the heat. Furthermore, fire gases normally present in a fire may constitute a hazard in themselves. Nevertheless, decomposition products are a definite source of difficulty that should not be overlooked.

SOURCES OF CONTACT WITH REFRIGERANTS

As long as refrigerants are confined properly there is no life, fire, or explosion hazard. On the other hand, if the refrigerant escapes, personal injury and property damage may occur.

Persons may come in contact with refrigerants (aside from their manufacture) in homes, business offices, industry, public assembly, and, in fact, any place where refrigerants are used. The danger may be to both life and property if the refrigerant is explosive; to life only if merely toxic. Refrigerants that are both toxic and irritating may create additional hazards by causing panic and also by hindering firemen in case of fire. Decomposition of refrigerants may produce toxic gases that create an additional hazard.

Contact of the general public with refrigerants may be considered as accidental; firemen may come in contact with them while fighting fires, and servicemen may have repeated contacts in the course of their employment. From the standpoint of toxicity, acute effects are the most significant except for servicemen and possibly employees working in close proximity to large refrigerating units, in which case chronic effects also may become important.

PREVENTION OF CONTACT WITH REFRIGERANTS

The safe use of refrigerants is based, therefore, upon preventing the escape of a hazardous quantity of refrigerant. The following are suggested as steps toward accomplishing this goal: (1) Use of properly designed, constructed, and tested equipment to minimize leaks; (2) limitation of amount of refrigerant; (3) choice of a refrigerant that presents a minimum of potential hazard for condition of use; (4) proper installation and safety devices; and (5) inspection and maintenance.

Although the order in which the suggestions are presented is not necessarily that of importance, preventing leaks appears to be a logical choice for first consideration because if mechanical equipment could be made 100 percent perfect, the problem of preventing dangerous quantities of refrigerants from escaping would be solved. Although much has been accomplished, leaks do occur, and other steps are therefore necessary.

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The hazard from refrigerants tends to increase with increase in amount of refrigerant used, because the possibility of producing dangerous concentrations over a greater area is increased. Decreasing the amount of refrigerant limits the area of dangerous contamination. In fact, a combination of steps (1) and (2) - good construction and limited quantity of refrigerant - to a large extent has overcome any significant hazard associated with individual units that use only a few pounds of refrigerant.

Limiting the quantity of refrigerant cannot be applied to any extent in commercial installations, and additional steps are necessary. However, the quantity of refrigerant used bears directly on the type of installation as well as precautionary measures taken. Choice of a refrigerant having the least potential hazard under the conditions of use is another step in safe use. The American Standard Safety Code for Mechanical Refrigeration classifies refrigerants into three groups, as follows:

Group 1

Carbon dioxide	CO_2
Dichlorodifluoromethane (Freon-12)	CCl_2F_2
Dichloromonofluoromethane (Freon-21)	$CHCl_2F$
Dichlorotetrafluoroethane (Freon-114)	$C_2Cl_2F_4$
Dichloromethane (Carrene No. 1) (methylene chloride)	CH_2Cl_2
Trichloromonofluoromethane (Freon-11) (Carrene No. 2)	CCl_3F

Group 2

Ammonia	NH_3
Dichloroethylene	$C_2H_2Cl_2$
Ethyl chloride	C_2H_5Cl
Methyl chloride	CH_3Cl
Methyl formate	$HCOOCH_3$
Sulfur dioxide	SO_2

Group 3

Butane	C_4H_{10}
Ethane	C_2H_6
Isobutane	$(CH_3)_3CH$
Propane	C_3H_8

Restrictions are given for use of the various refrigerants in each group that relate to item (4), installation precautions and safety devices. As these points are described in detail in the code they are not presented here. They

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pertain to such items as type of installations (direct or indirect), proper machinery room, fire-resistant shafts, automatic fire dampers, high-pressure cut-outs, and safety plugs.

Last and certainly not least are periodic inspections and maintenance. These should be basic requirements for all equipment associated with health or safety hazards and can hardly be overemphasized.

PERSONAL PROTECTIVE DEVICES

Although only general safety measures can be recommended for the vast majority of persons who might be exposed to refrigerants, specific personal protection can be recommended for certain groups, such as firemen and repairmen, and for emergency situations.

As firemen may be exposed to a variety of toxic gases they are generally equipped with the universal gas mask or oxygen breathing apparatus. As they are trained in the use and limitations of these devices, they are not discussed further.

For emergency purposes, proper respiratory protective devices should be available in accessible places, and persons likely to be called upon to use them should be thoroughly instructed in such use. The devices should be inspected at regular intervals and kept in first-class condition.

Repairmen may be called upon during an emergency, or they may be exposed to relatively low concentrations at frequent intervals during general repair work with the possibility of experiencing chronic effects. For protection against the latter hazard, precautions should be taken to keep the concentration of refrigerant in the breathing zone at a minimum. This can be accomplished by allowing the gases to escape slowly, by absorbing them in suitable mediums, working in hoods, or using other suitable methods of ventilation. If necessary, suitable respiratory protection should be provided. Goggles also should be worn by persons handling refrigerants.

CHANGING REFRIGERANT

One other point should be emphasized. There is always the possibility of recharging a system with a refrigerant other than that for which the system was designed. This is particularly likely to happen during the present emergency. Substituting one refrigerant for another is dangerous practice and should not be done without careful consideration of all factors and consultation with the manufacturer of the equipment.

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SUMMARY

Safe use of a refrigerant depends on knowledge of its pertinent properties and conditions of use. Data on the properties of refrigerants serve as a basis for the following suggested control measures: (1) Use of properly designed, constructed, and tested equipment to minimize leaks; (2) limitation of quantity of refrigerant; (3) choice of refrigerant that presents a minimum of potential hazard for conditions of use; (4) use of proper installation and safety devices; and (5) inspection and maintenance.

Personal protective devices should be provided when necessary.

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